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(54) **Granular laundry compositions.**

(57) Granular laundry compositions comprising a particulate mixture of a water-insoluble natural or synthetic silica or silicate, a finely-divided organic peroxy acid bleach precursor, and an alkoxylated nonionic surfactant. The particulate mixture has a pH in 2% aqueous dispersion of from pH 2 to pH 9. The compositions have improved granular physical characteristics, chemical stability and rate of solution/dispersion characteristics. They are useful in bleach activator, bleaching, detergent and laundry additive compositions.

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GRANULAR LAUNDRY COMPOSITIONS

The present invention relates to granular laundry compositions. In particular it pertains to compositions containing activators for oxygen-releasing compounds, especially activators in the form of organic peroxyacid bleach precursors. The laundry compositions are useful as bleach activator compositions, bleaching compositions, detergent compositions, laundry additive compositions and the like. As used herein, the terms bleach activator and organic peroxyacid bleach precursor are used synonomously.

It is well known that peroxygen bleaching agents, e.g., perborates, percarbonates, perphosphates, persilicates etc., are highly useful for chemical bleaching of stains found on both colored and white fabrics. Such bleaching agents are most effective at high wash solution temperatures, i.e., above about 70°C. In recent years, attempts have been made to provide bleaching compositions that are effective at lower wash solution temperatures, i.e., between room temperature and 70°C. In consequence, bleaching agents have been investigated which exhibit their optimum bleach activity in this temperature range. These low temperature bleaches are useful in a variety of products intended for use under machine or hand-wash conditions, e.g., additive pre-additive or soak-type laundry compositions as well as all-purpose detergent compositions.

A very effective class of low temperature bleach system comprises a peroxy bleach compound and an organic peroxyacid bleach precursor which react together to form the organic peroxyacid bleach in the wash solution. Examples of detergent compositions incorporating bleaching agents of this type are disclosed in U.S.P. 2,362,401 (Reicher et al), U.S.P.

3,639,248 (Moyer) and in British Patent No. 836,988 and 855,735.

It is well-known, however, that bleach-activator containing detergent compositions suffer a number of technical problems which until now have limited their commercial applicability and market success. The underlying problem is that of activator instability, i.e., the tendency of the activator to degrade by hydrolysis and perhydrolysis reactions under the alkaline and oxidizing conditions typically encountered in detergent compositions during storage. This leads not only to loss of bleaching efficacy but also to degradation of other sensitive ingredients in the detergent formula, for example perfumes, optical brighteners, enzymes, dyes etc.

In the art, two major approaches have been used to tackle the instability problem. In the first approach, the activator is protected from its hostile alkaline/ oxidizing environment by agglomeration, coating or encapsulation with a non-hygroscopic, preferably hydrophobic agglomerating, coating or encapsulating material (see for instance U.S.P. 3,494,786 (Neilson), U.S.P. 3,494,787 (Lund and Neilson) and U.S.P. 3,441,507 (Scheifer)). This technique suffers the disadvantage, however, that to be efficaceous, the agglomerating or coating material must be so water-impervious as to considerably inhibit the rate of release of bleach activator into the detergent wash liquor. This leads to diminished bleach effectiveness and increased cost. Where, on the other hand, a hydrophilic agglomerating or coating agent is used, for instance, a water-soluble nonionic surfactant, the hygroscopicity of the product is such that no meaningful improvement in activator stability can be achieved. This is particularly true where high levels of nonionic surfactant are included in the granule, for instance, levels in excess of about 15% by weight.

In the second approach to improving activator stability, the activator is incorporated in the detergent composition in the form of relatively coarse-sized particles (see, for instance, U.S. Patent 4,087,369), the object being to reduce interaction of the activator with its environment by minimizing the surface/unit weight of the activator. This approach suffers the disadvantage, however, that the rate of dispersion and solubilization of the activator is so slow as to considerably increase the risk of fabric damage known as "pinpoint spotting". In essence, "pinpoint spotting" is a local bleach effect caused by slow dissolution of individual particles of the bleach system resulting in a locally high concentration of the bleaching agent at the fabric surface. High solubilization rate is thus seen to be critical for avoiding problems of damage to fabrics, but in as much as high solubilization rate has traditionally implied either a high activator surface/unit weight or agglomeration with a hygroscopic agglomerating agent, it follows that the twin aims of improving fabric safety and activator stability have been to a large degree mutually exclusive.

The present invention seeks, as one of its objectives, to resolve these conflicing requirements by providing a matrix of materials in particulate form that has excellent granular physical characteristics, activator stability and rate of solution/dispersion characteristics; that delivers these benefits in a composition comprising high levels of detergent functional nonionic surfactants; and which also delivers these benefits in a detergent composition prepared from highly alkaline and oxidizing detergent components.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a granular laundry composition comprising from about 0.5% to 100%, preferably from about 5% to 100%, by weight of a particulate mixture having a pH in 2% aqueous dispersion of from 2.0 to 9.0 and comprising:-

(a) a finely-divided, water-insoluble natural or synthetic silica or silicate,

(b) a finely-divided organic peroxy acid bleach precursor, and

(c) an alkoxylated nonionic surfactant.

The natural or synthetic silica or silicate has an average primary particle size of less than about 10μ and a moisture content of from about 0.1% to about 30% by weight thereof, and is in admixture with the bleach precursor having an average particle size preferably less than about 500μ in a weight ratio of from about 20:1 to 1:10. The weight ratio of silica or silicate to nonionic surfactant falls in the range from about 20:1 to 1:3. The particulate mixture preferably has an average particle size of from about 250μ to about 3000μ, more preferably from about 500μ to about 2000μ.

The bleach activator is thus incorporated in a matrix of water-insoluble silica or silicate and alkoxylated nonionic surfactant, both of which classes of materials can be hydrophilic in nature, but which in the particulate mixture interact to provide an intrinsically hydrophobic, non-hygroscopic complex. The hydrophobicity of the particulate mixture can be determined by measuring the weight % of moisture-pickup of granules of the mixture after 72 hours storage at 32°C and 80% relative humidity. Preferably, the moisture-pickup under these conditions is less than about 6%, more preferably less than about 3.5% and desirably less than about 1.5% by weight of the particulate mixture.

It should be understood that "moisture-pickup" here refers to the weight of moisture gained by the particulate mixture rather than to the absolute level of water contained therein. Absolute moisture content is, of course, one factor determining the moisture-pickup level, other determining factors including the hygroscopicity of the silica or silicate and the nonionic surfactant, the physiochemical interaction of silica or silicate and the nonionic surfactant, and the weight ratio of the two types of material in the particulate mixture. For a giv n surfactant/silicate pair, the important

factors determining moisture-pickup are thus absolute moisture level and the weight ratio of surfactant to silicate. These two factors are also important from the viewpoint of granulometry, however, i.e., they determine granule average size, size distribution, flow characteristics etc. Thus for a given surfactant/silicate pair, both the absolute moisture content and the ratio of surfactant to silicate should be adjusted within the broad limits specified above to provide granules having optimum granulometry and minimum moisture-pickup.

With regard to the water-insoluble silica or silicate, this preferably has an average primary particle size (i.e. number average particle diameter for the primary crystals or primary aggregates as obtained, for instance, from electron microscope measurements) of less than about 4 μ, more preferably less than about 1 μ, and a pore volume (as obtained for instance, by water adsorption under A.S.T.M. C-20-46) of at least 0.1 cc/g, more preferably at least 0.2 cc/g. Preferably also, the silica or silicate has a pore volume for cavities within the range from 400 Å to 2.5 μ of at least 0.05 cc/g (measured in a mercury porosity meter) and an external surface area (measured, for instance, by dye adsorption) of at least 5 sq. metre/g, more preferably at least 15 sq. metre/g.

With regard to chemical composition, the water-insoluble silicate is preferably a sheet-like, natural clay, especially a clay selected from the smectite-type and kaolinite-type groups. Highly preferred from the viewpoint of granulometry, processibility, moisture-pickup, activator stability, and dispersibility are the three-layer expandable clays of the smectite-group, especially alkali and alkaline earth metal montmorillonites, saponites and hectorites. Desirably, these have a moisture content in the range from about 8% to about 20%. Kaolinite-type materials such as kaolinite itself and calcined kaolin and metakaolin are also suitable however. In these cases, moisture content generally lies in the range from about 0.1% to about 18%, more preferably from about 0.3% to about 12%.

BAD ORIGINAL

Other suitable water-insoluble silicates include aluminosilicates of the zeolite type, particularly those of the general formula:-

$$Na_z\ (AlO_2)_z\ (SiO_2)_y\ xH_2O$$

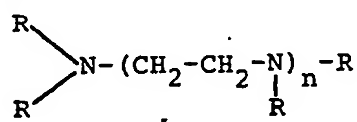
wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5 and x is a number such that the moisture content of the alumino-silicate is from about 10% to about 28% by weight. Particularly preferred materials of the zeolite class are those prepared from clays themselves, especially A-type zeolites prepared by alkali treatment of calcined kaolin.

The alkoxylated nonionic surfactant is preferably selected to have an average HLB in the range from about 9.5 to 13.5 and to have a melting point of no more than about 32°C, more preferably about 28°C; these conditions are found to provide granules having the optimum combination of hydrophobicity and water-dispersibility. Highly suitable nonionic surfactants of this type are ethoxylated primary or secondary C_{9-15} alcohols having an average degree of ethoxylation from about 3 to 9.

The water-insoluble silica or silicate, peroxy acid bleach precursor and nonionic surfactant preferably constitute from about 15% to 60%, 5% to 80% and 5% to 40%, more preferably from about 20% to 60%, 5% to 40% and 20% to 40%, of the particulate mixture, respectively. In other words, the particulate mixtures are adapted to contain relatively large amounts of the functional activator and detergent components of the composition in relation to the silica or silicate. Desirably, however, the particulate mixture is essentially free of inorganic per-compounds which yield hydrogen peroxide in water, e.g. sodium perborate tetrahydrate.

The pH characteristics of the bleach activator/silicate/nonionic surfactant matrix is also highly important, and critically, the particulate mixture should have a pH in 2% aqueous dispersion of the particulate mixture of from about 2 to about 9.0, preferably from about 3 to about 8.5, especially from about 4 to about 7. If necessary, optimization of the pH to within the above range can be effected by means of a separate pH regulating agent. Control of pH is important for stabilizing the activator against hydrolytic and perhydrolytic degradation and is particularly effective in this respect in the moisture-controlled environment of the hydrophobic granule.

A further highly preferred though optional component of the composition is a polyphosphonic acid or salt thereof, particularly those having the general formula:-



in which n is an integral number from 1 to 14 and each R is individually hydrogen or $CH_2PO_3H_2$ or a water-soluble salt thereof, provided that at least half of the radicals represented by R are $CH_2PO_3H_2$ radicals or water-soluble salts thereof. Especially preferred are diethylene triamine penta (methylene phosphonic acid); ethylene diamine tetra (methylene phosphonic acid) and salts thereof. These can be included either in the particulate mixture or in the remainder of the composition in levels of from about 0.5% to about 10%, preferably about 1% to about 5% by weight of the particulate mixture or about 0.1% to 4% by weight of the total composition. The polyphosphonates have been found to be uniquely effective in stabilizing organic peroxyacids against the generally deleterious effect of water-insoluble silicates, especially those belonging to the zeolite and kaolin classes. Accordingly, a highly preferred embodiment of the invention is a granular detergent composition comprising from about 0.5% to 100% of a particulate mixture comprising:-

(a) a finely-divided, water-insoluble natural or synthetic silica or silicate having an average primary particle size of less than 10μ and a moisture content of from 0.1 to 30%, and

(b) a finely-divided organic peroxy acid bleach precursor in a weight ratio of (a) to (b) of from 20:1 to 1:10, and wherein the composition additionally comprises

(c) a polyphosphonic acid or salt thereof as defined above, the weight ratio of (a) to (c) falling in the range from 100:1 to 1:1.

Another highly preferred component of the composition of the invention is a water-soluble cationic surfactant which is incorporated in the particulate mixture in a level from about 5% to about 40% thereof. Especially suitable water-soluble surfactants have the general formula:-

$$R^1_m \; R^2_{4-m} \; N^+ \; Z$$

wherein R^1 is selected from C_{8-20} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_{1-4} alkyl, and benzyl groups; Z is an anion in number to give electrical neutrality; and m is 1, 2, or 3, provided that when m is 2, R^1 has less than 15 carbon atoms and when m is 3, R^1 has less than 9 carbon atoms.

Apart from providing a detergency function, the water-soluble cationic surfactant also contributes towards reducing moisture-pickup and improving the granulometry of the particulate mixture.

The granular detergent composition can consist solely of the particulate mixture, in which case the composition is designed for use primarily as an additive product simultaneously with a conventional bleach-containing detergent composition, or it can consist of a combination of the particulate mixture with conventional auxiliary detergent components. In the latter instance, a preferred composition comprises:-

(a) from about 0.5% to about 60%, preferably from about 5% to about 60%, of the particulate mixture, and

(b) from about 40% to about 99.5%, preferably from about 40% to about 95%, of auxiliary detergent components in powder form comprising:-

(i) about 5% to about 35% of an inorganic per-compound, yielding hydrogen peroxide in water,

(ii) about 1% to about 30% of an anionic surfactant, optionally in combination with a nonionic, cationic, zwitterionic, ampholytic surfactant or mixture thereof, and

(iii) about 2% to about 93.5%, preferably about 2% to about 89% of a detergency builder.

In a method of making the compositions of the invention, the alkoxylated nonionic surfactant is dispersed in liquid form onto a moving bed of a mixture of the water-insoluble silica or silicate and organic peroxy acid bleach precursor to form agglomerates which are then admixed with the auxiliary detergent components, if any, of the composition. The process can be performed in, for instance, a pan agglomerator, Schugi mixer or fluidized bed apparatus.

The various components of the compositions of the invention will now be discussed in more detail.

THE WATER-INSOLUBLE SILICA OR SILICATE

As described earlier, the water-insoluble silica or silicate is preferably a mineral clay selected from the smectite-type and kaolinite-type groups.

There are two distinct classes of smectite clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in the outer layers. The dioctahedral minerals are primarily trivalent metal ion-based clays and are comprised of the prototype pyrophyllite and the members montmorillonite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Mg_x)O_{20}$, nontronite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Fe_x)O_{20}$, and volchonskoite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Cr_x)O_{20}$, where x has a value of from 0 to about 4.0 and y has a value of from 0 to about 2.0.